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PROCESSES FOR MAKING BARIUM AND ITS ALLOYS

BY

W. J. KROLL

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PROCESSES FOR MAKING BARIUM AND ITS ALLOYS[1]

By W. J. Kroll[2]

INTRODUCTION

Despite the fact that barium minerals are plentiful and widely distributed in nature, this element is one that we do not yet know how to prepare cheaply in metallic form. This is due to its chemical activity, as evidenced by its great affinity for fluorine, chlorine, oxygen, nitrogen, hydrogen, and sulfur. Furthermore, it forms a very stable subchloride and subfluoride, which prevents isolation of the metal by fusion electrolysis from a halide bath. A good survey of the metallurgy of barium, calcium, and strontium has been made recently in Light Metals (54,55).[3]

Metallic magnesium (46), calcium (83), barium, and strontium (27) reduce each other's oxides. Proof of this can be found in the activation of BaO after reduction with Mg, which leads to the formation of so-called "Maquenne" mixtures (58) used for absorbing gases. However, it is impossible to extract the reduced metal from the residue, a fact that Guntz (25) attributed to the formation of barium suboxide. There is no necessity for presuming the formation of such a compound, as it has been established that in the reduction there is always formed an alloy of the alkaline-earth metal with the magnesium, which is capable of producing hydrogen when brought into contact with water. The reduction of alkaline earth-metal oxides with aluminum was observed by Mallet (57) in 1877, but recent investigations have shown that the end product of the reaction is an alloy of aluminum with the alkaline earth metal (1,2). Silicon also has been suggested as a reducing agent, and the results obtained are the same (84,85).

Gunts (26,28) worked out a method for the removal of the reduced alkaline-earth metal, which consisted in heating the residue under a vacuum. The alkaline-earth metal is thus distilled off and condensed in a cool part of the apparatus. This method was applied to the reduction of magnesia by Matignon (59), who later suggested using silicon (60) as the reducing agent for BaO. The present silicon-dolomite process of magnesium production is based upon the work of Matignon, who in the last war tried unsuccessfully to reduce magnesia with carbide and aluminum on a commercial scale. He proposed the use of CaF_2 (61) as an activator and mentions the possibility of employing dolomite. He failed owing to lack of heat-resisting steel retorts, which were not available at that time.

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[2] Consulting metallurgist, Bureau of Mines, Albany, Oreg.

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The principles involved in the reduction of BaO with other metals apply also to the reduction of SrO, CaO, MgO, and, with some restrictions, Li_2O. As to the reducing agents, Ti, Zr, Th, Ta, Cb, V, Be, and even W and Ni have been found suitable in specific instances. In the present investigation, experiments are confined to the reduction of barium oxide with aluminum or silicon. Other metals are discussed in a general way to give the reader a broader knowledge of the subject.

PHYSICS AND CHEMISTRY OF THE GUNTZ PROCESS

Barium melts at 710°C. and boils at 1,500°C (80). It is the least volatile of the alkaline-earth metals. Its vapor pressure at 1,200°C (the temperature of its reduction from the oxide) is about 50 mm. Hg, which is far more than is required for rapid evaporation of the metal. At this temperature, the actual pressure of barium vapor above the reaction mixture is probably of the same order as that found by Schneider (73) above the silicon-magnesia mixture, namely, about 2 mm. Hg, which is sufficient for commercial operation.

The Guntz process consists of heating 3 BaO with 2 Al in a vacuum at about 1,200°C. and condensing the barium vapor in a cool end of the tube. Matignon (60) later suggested using silicon instead of aluminum, or a 90-percent ferrosilicon, which is cheaper but requires a temperature of operation 50°C. higher than that necessary with aluminum. Analogeous results obtained with aluminum instead of ferrosilicon in the dolomite-magnesium process have been published recently (68).

For simplicity, the reduction mechanism of the Guntz process will be examined where silicon and aluminum are employed as reducing agents, as more reliable literature data for the chemical compounds of these agents are available.

Woehler (85) has shown that barium oxide is readily reduced by silicon with formation of a 35-percent Ba-Si alloy containing $BaSi_3$ in an excess of Si. At higher temperature, obtained by using BaO_2 (63,64), products with a higher barium content can be obtained, and it is claimed that silicides containing 50 percent Ba can be made in the arc furnace (42,43). Woehler studied the properties of the silicides of barium and found that the compound $BaSi_3$ with 62 percent Ba does not evolve barium when heated in a vacuum at 1,200°C, and cannot be hydrided, whereas, the silicide Ba_2Si_2, like Ca_2Si_2 (56,84,85), does both. This indicates that the silicides with a barium content higher than that of $BaSi_3$ have "loose" barium atoms. The heat of formation of $BaSi_3$, according to Woehler, is 399.2 Cal. This figure, by comparison, is much higher per atom of Ba than that of BaO, which is 133.1 Cal. However, all silicides of the alkaline-earth metals are thermally dissociated at elevated temperature, as they can be split by iron,

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with production of FeSi, having a heat of formation of only 19.2 Cal (67). This heat of formation is still largely available at elevated temperature, as proved by the fact that molten iron, when alloyed with silicon, becomes hotter. Aluminum behaves similarly.

Barium oxide can readily be reduced by aluminum, and alloys containing 36.0 percent Ba have been made in this way (1,2). Barium peroxide can be flashed with aluminum powder, yielding alloys with up to 60 percent Ba (76). A compound, Al_4Ba, is formed that contains 56 percent Ba and dissolves in excess aluminum. Nothing is known about the beat of formation of this compound, but it can be split with iron at elevated temperature, as the iron aluminide is thermally more stable than barium aluminide.

The relation of reducing agent to oxide in the reaction mixture is important. Guntz (26,28) suggested the use of 3 BaO plus 2 Al to form only Al_2O_3. Matignon (60) already recognized the necessity of forming double oxide compounds. He suggested using 3 BaO with 1 Si to produce barium metasilicate. However, as the efficiency obtained was only about 50 percent, it is evident that the conditions for obtaining orthosilicate prevailed. According to Gire (19,21), conditions for forming the orthosilicate exist when reducing dolomite with silicon, as two molecules of CaO are liberated. Despite these facts, the use of orthosilicate-forming mixtures has been patented again (35,39).

The chemistry of the Guntz process, in which monaluminate or orthosilicate is produced, can be represented by the following equations:

Silicon reduction

1. $4\ BaO + Si = SiO_2.2\ BaO + 2\ Ba.$
2. $4\ BaO + 7\ Si = SiO_2\ .\ 2\ BaO + 2\ BaSi_3$
3. $Ba + 3\ Si = BaSi_3.$
4. $12\ BaO + BaSi_3 = 3\ (SiO_2.2\ BaO) + 7\ Ba.$

Aluminum reduction

1. $4\ BaO + 2\ Al = BaO.Al_2O_3 + 3\ Ba$
2. $4\ BaO + 14\ Al = BaO\ .\ Al_2O_3 + 3\ BaAl_4$
3. $Ba + 4\ Al = BaAl_4.$
4. $8\ BaO + BaAl_4 = 2\ (BaO.Al_2O_3) + 7\ Ba.$

Recent investigations of Weyer (82), Grube and Trucksess (23), Jander and Wuhrer, (44), Schneider and Hesse (73), and Taylor and Williams (78) prove that when mixtures of alkaline-earth metal oxides, including MgO, are heated with silica in any proportion, even with excess of the latter, there is first formation of the orthosilicate, whereas mixtures with alumina form first monoaluminate (22). According to Jander and Wuhrer (44), a mixture of $BaO\text{-}SiO_2$ gives, in 10 hours at 1,010°C., a reaction product with only 10 percent $BaO.SiO_2$, but 70 percent $2\ BaO.SiO_2$, the former being produced in a secondary reaction with the excess of SiO_2 and the orthosilicate.

The preferential formation of orthosilicate has been explained by the greater speed of crystallization of this compound, which produces more nuclei than the metalsilicate. It is also said that the alkaline-earth oxide diffuses faster through ortho- than through metasilicate. Weyer (82) gives a picture of the diffusion mechanism in which the silica nucleus is surrounded by a thin layer of metasilicate contained in orthosilicate. It is indeed difficult to understand the operation without admitting the presence of metasilicate at the interface of the silica.

These basic data can be used to explain the reaction between silicon and the oxide of an alkaline-earth metal. A silicon particle starts reacting with the alkaline-earth metal oxide, which is present in a large excess in the beginning. A metasilicate film is produced at the interface, from which orthosilicate forms with more oxide. Through this layer, more oxide diffuses, and more orthosilicate grows from the interface to which silica is supplied by diffusion through the skin of metasilicate. The orthosilicate is reducible to metasilicate and metal, but the metasilicate is stable against silicon. Therefore, the metasilicate film is continually built up to orthosilicate with diffusing oxide and reduced back by contact with the silicon. This takes place only at the interface, and orthosilicate grows in the direction opposite to the flow of the oxide. The diffusion of alkaline-earth metal oxide through the orthosilicate is the main element that rules the speed of the reaction. Additions of materials such as CaF_2, which act as mineralizers, may also have an influence on the rate of diffusion. Other fluorides and chlorides have been suggested (33,68) to reduce the reaction time or to increase the yield for a given temperature. Equations 1, given above, summarize these facts.

According to equation 2, silicon reduction, there is formation of barium silicide besides orthosilicate, and equation 3 indicates that liberated barium reacts back with silicon and forms silicide. There can be no doubt about the production of silicide, as this is the method used by Woehler in making this compound. However, only a thin layer of the silicide may be formed on the surface of the silicon particles owing to the slowness of the diffusion, the melting point of the alloy depending on the composition. At the high temperature of operation, this alloyed layer may be melted, thus speeding up the reaction by wetting of the reaction mixture. The silicide layer reacts with BaO, according to equation 4, with liberation of barium. Danner (15) employs reaction 4 exclusively in reducing BaO at atmospheric pressure with aluminum, producing aluminide, and continuing the reduction with this aluminide and residual barium oxide by heating the reaction mixture in a vacuum at elevated temperature. The sieving-out he recommends before the second step can not increase the yield, as the aluminide, like the silicide, is stable in a vacuum at high temperature.

The aluminum reduction, as shown by equations 1 to 4, proceeds a little differently from that with silicon, insofar as monoaluminate is formed first. This has been shown by Grube and Heintz (22), and some patents refer to it (35,37). We presume that monoaluminate is not reducible by aluminum at the temperature of operation, but dialuminate

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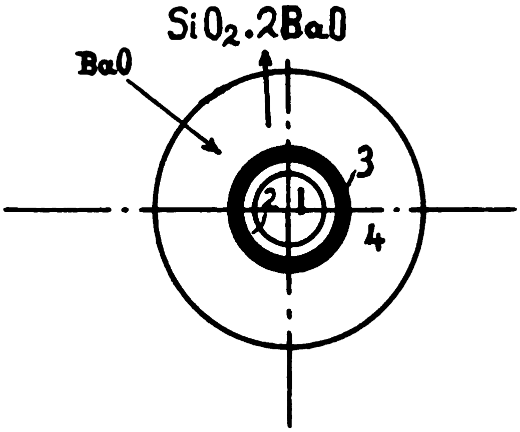

FIGURE I

1. Si particle
2. Barium silicide layer
3. Skin of $BaO \cdot SiO_2$
4. $SiO_2 \cdot 2BaO$

certainly is, as indicated in the Ivanow plant (41). The reactions may therefore be summarized as follows: Aluminum reacts with formation of aluminide, which is completely melted at the temperature of operation and therefore wets the mixture. Monoaluminate is produced at the interface through which excess barium oxide diffuses. It grows into the space opposite the direction of the diffusion.

Schneider and Hesse (73) claim that the volatile compound SiO silicon monoxide interferes with the reduction of MgO with silicon. Although the existence of silicon monoxide is fairly well proved (86-88), it is rather doubtful whether it could form in the presence of barium vapor, which would break it down to orthosilicate and barium silicide. In the reduction with aluminum, no such compound can form, which shows that there is no necessity for assuming its action in the silicon reduction.

In the above equations, no consideration was given to the hypothesis of Guntz that barium suboxide is formed as an intermediary product. Schriel (74) examined this possibility and concluded that suboxide does not exist but that barium dissolves its own oxide to a large extent. The evaporation of Ba from BaO becomes increasingly difficult with mixtures containing less than 2.5 mol barium per mol BaO.

An illustration of the above-described phenomenon is given in figure 1. As to the reduction of dolomite with silicon, somewhat different conditions have to be taken into account. The end product of the reaction is calcium orthosilicate; but there are cross reactions resulting in the intermediary formation of double silicates of magnesium and calcium. Some of these melt at temperatures as low as 1,321°C., and diffusion must be speeded under these conditions. As to the possible formation of Mg_2Si, it is known that magnesia can be reduced at high temperature by silicon, but as magnesium boils at 1,104°C, all depends on the thermal stability of Mg_2Si. It is known that this compound remains behind when magnesium is sublimed at about 650°C. in a perfect vacuum (31), but it has also been shown that the compound is at least partly dissociated at its melting point of 1,102°C. at atmospheric pressure. Comparison with the conditions prevailing in the magnesium-lead system indicates that some magnesium stays behind at temperatures above the boiling point of magnesium. Leitgebel (53) found that the boiling point of a 20-percent MgPb alloy is 1,218°C., and it can therefore be supposed that silicon, too, lowers the vapor pressure of magnesium. How much magnesium will be retained on the surface of the silicon particles at 1,150°C, which is the temperature of operation in the dolomite-magnesium process, in a vacuum of about 2 mm. corresponding to the vapor pressure of the magnesium in the reaction zone, cannot be foreseen. It would be necessary to investigate the thermal dissociation of Mg_2Si before making any conclusions. The analogy with the barium oxide reduction with silicon is apparent, however.

On the basis of the above equations, some improvements of the Guntz process could be suggested. As the operation proceeds mainly by way of equation (4), which shows that BaO is reduced by the silicide, it would

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seem advisable to start directly from a silicide-BaO mixture. However, the barium silicide of commerce is of low grade, about 35 percent Ba, and losses are to be expected in the grinding operation, because the barium silicide in opposition to $CaSi_2$ is not stable in air. Analogous conclusions can be made for the use of aluminide.

Guntz (24) suggested using additions of $CaSi_2$, but he mentions that the resulting barium is contaminated with calcium. It is possible that additions of CaO could be used to tie up some of the silica as calcium orthosilicate instead of forming barium orthosilicate with the purpose of using less of the more expensive barium oxide. Calcium oxide is more difficult to reduce with silicon than BaO, but, according to Guntz, some contamination of the barium with calcium must be expected when a BaO-CaO mixture is used. This proposition may work with strontium, however, which is much more volatile and easier to reduce than calcium. Calcium itself, according to Guntz (27), is a good reducing agent for strontium.

The addition of BaO_2 when reducing BaO with Al or Si is common practice and is said to increase the efficiency, doubtless due to higher temperature obtained. Although its effectiveness is assured with aluminum at atmospheric pressure, its usefulness in a vacuum, mainly in combination with silicon, is rather questionable. LaChatelier (52) has shown that the oxygen pressure over BaO_2 is 20 mm. Hg at 525°C., and it is therefore probable that most of the oxygen is given off by thermal dissociation in the vacuum of the reaction vessel before reaching a temperature at which it can react with the aluminum. Furthermore, a flash, such as may occur when using BaO_2, is undesirable, as it causes local overheating, sintering, and dusting. Additions of Fe_3O_4 have been proposed (13) but are open to the same objections.

The Guntz process has been applied successfully to the reduction of other alkaline-earth metal oxides. It is indeed easier to make strontium (26) by this method than barium. Calcium oxide is much more difficult to reduce with silicon or aluminum than BaO, according to Biltz and Hohorst (4) and Biltz and Wagner (6) but some patents (33,36,38-40) refer to methods for facilitating the reduction. As shown above, the process proceeds by way of a silicide or aluminide formation, and these compounds react with excess CaO forming double oxide compounds with liberation of Ca. The calcium silicide and aluminide have a much lower heat of formation than the corresponding barium compounds, namely 51.0 Cal. for Al_3Ca, according to Biltz (3) and 161.5 Cal. for $CaSi_2$, according to Woehler and Muller (84) and Woehler and Schuff (85). This should facilitate the reduction. A 50-percent calcium-aluminum alloy can readily be made in an electric furnace (8, 32, 47, 75), and such a high-grade material would be a suitable reducing agent for CaO in vacuo.

OTHER METHODS FOR MAKING BARIUM METAL

Inventors of Dow Chemical Co. proposed three different reactions for making calcium in a vacuum at high temperature, which may also be suitable for making barium. They are the displacement of calcium by iron in the silicide (30), the reaction of carbide with silicide (29,81), or with silicon, with formation of silicon carbide and liberation of calcium. With respect to barium, the corresponding equations may be written as follows:

1. $BaSi_3 + 3\ Fe = 3\ FeSi + Ba$.
2. $BaC_2 + 2\ Si = 2\ SiC + Ba$.
3. $3\ BaC_2 + 2\ BaSi_3 = 6\ SiC + 5\ Ba$.

Despite the fact that FeSi has a heat of formation of only 19.2 Cal. (67), the reaction works with calcium silicide, according to these inventors. The heat of formation of SiC is the decisive element of both equations 3 and 4, which is given by Ruff and Geiger (71) as 26.7 Cal. and by Brunner (7) as 43.5 Cal. All depends on the thermal stability of the compounds that participate in the reaction. Elementary silicon reacts with carbon at 1,400°C. (62), which is also the temperature recommended for the above Dow process. Such a temperature is impracticable in commercial vacuum furnaces.

The electrolysis of fused $BaCl_2$ does not yield any metal but only subchloride (24). Knowing that subchloride reacts with lead, forming BaPb, molten $BaCl_2BaF_2$ was electrolyzed by the author with a soluble molten barium-lead anode containing 8 percent Ba in an inert gas atmosphere, using a contact cathode. No barium was obtained.

Strontium (66,79) is easily made by electrolysis of the fused chloride mixed with KCl.

Caron (9,10) made barium-zinc by reaction of $BaCl_2$ with sodium zinc, and he claims that he obtained barium metal by distilling off the zinc.

Guntz (24) and Gauthier (18) have shown that cadmium barium made by fusion electrolysis yields a fairly pure barium in a vacuum at high temperature.

Guntz (24) also used amalgam made either by aqueous electrolysis or by reaction of sodium amalgam with concentrated $BaCl_2$ solution. However, the mercury can not be driven off completely by the vacuum treatment with application of heat. About 0.2 percent Hg remain behind (69), which makes the metal unfit for getter purposes.

Guntz (24) also dissociated hydride made from cadmium alloy by heating in hydrogen while driving off the cadmium, but it is questionable whether all the hydrogen can be driven off from the hydride.

All the methods using metal solvents for the barium have the disadvantage that low-grade alloys have to be submitted to the dissociation procedure at fairly high temperature in a good vacuum. The alloys always pick up some oxide, which stays behind in the barium metal.

METHODS FOR MAKING BARIUM ALLOYS

Alberti (1,2) made a 36-percent barium aluminum alloy by reacting BaO in a $BaCl_2$ flux with aluminum. Woehler and Schuff (85) prepared a 33-percent silicide by reacting silicon with BaO/BaO_2. The writer obtained barium lead alloy by reduction of BaO with carbon in the presence of lead or by decomposing BaC_2 with lead in the absence of air (50). Alloys with 8 percent Ba can be made in this way. The method can also be used for preparing tin, antimony, and other heavy-metal barium alloys. When heated in presence of BaC_2 to a temperature of 1,400°, copper takes up 1.5 percent Ba.

Barium chloride is a suitable raw material for the production of barium alloys. It is not reduced by magnesium, and sodium makes subchloride (24). In the presence of hydrogen, sodium reduces $BaCl_2$ to hydride, which dissolves in the chloride. Sodium can be used to make barium alloys by the reduction of $BaCl_2$ in the presence of other metals (49), which may either be alloyed with the sodium or mixed with it. In this way, Caron made barium and zinc or lead alloys (9-11). Light-metal alloys, especially those with magnesium and aluminum, containing 30 percent Ba, can be made by the Caron process, but an inert gas seal is necessary. The alloys pick up a little sodium, which can be driven off at high temperature in a vacuum or by reaction with more chloride. The salt composition has to be adjusted in such a way that a fluid bath results after the reaction is completed. Most of the reactions given by Caron have not yet been investigated, and a study of the equilibria involved may be of interest. They comprise the whole group of alkali and alkaline-earth metals.

Calcium is also a suitable reducing agent for barium chloride. Muthmann, Weiss, and Metzger (65) reduced $BaCl_2$ with Ca and obtained a Ba-Ca alloy. The writer repeated this experiment and readily made a 38-percent barium alloy, which by a vacuum treatment was brought up to 58 percent Ba. This alloy could easily be pressed to wire at 400°C. Magnesium-barium alloys can be freed of their magnesium by a similar treatment. The equilibrium 2 LiCl-Ba has been studied by Jellinek and Czerwinski, (45).

Although such light-metal barium alloys may some day find practical applications, their use as getter metal is made impossible by the presence of small amounts of chloride. Any barium metal made from these alloys tenaciously retains chloride, which can not be removed by the vacuum treatment.

The fusion electrolysis with heavy metal cathode, in which the heavy metal may be introduced also as salt or taken from a subsidiary soluable anode, has frequently been employed for making barium alloys. In this way, Kornilow (48) obtained an 11-percent Ba/Zn alloy. The well-known Frary (14) metal of the last war, which contained about 2 percent Ba, some calcium, and the balance lead, was made in a similar way. Ray (70) showed how to make barium alloys with 73 percent Sb, 72 percent Sn, 84 percent Bi, and 97 percent Al, respectively, by fusion electrolysis with a heavy-metal cathode.

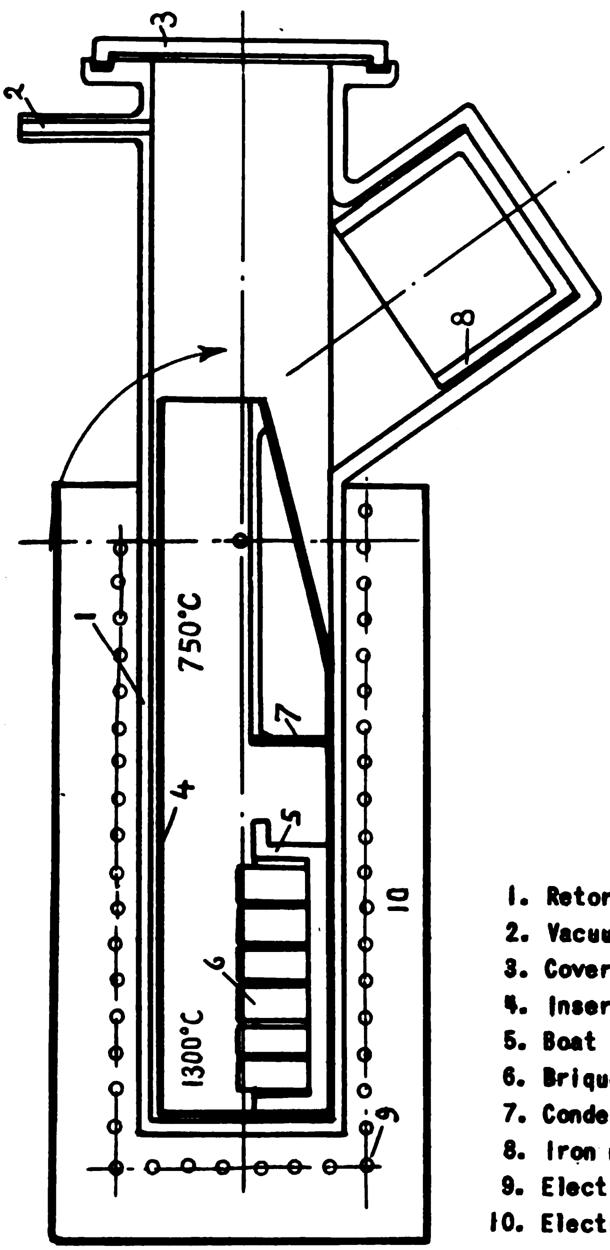

FIGURE 2

1. Retort
2. Vacuum connection
3. Cover
4. Insert
5. Boat
6. Briquettes
7. Condensor with liquid barium
8. Iron mold
9. Electric furnace coil
10. Electric furnace refractory

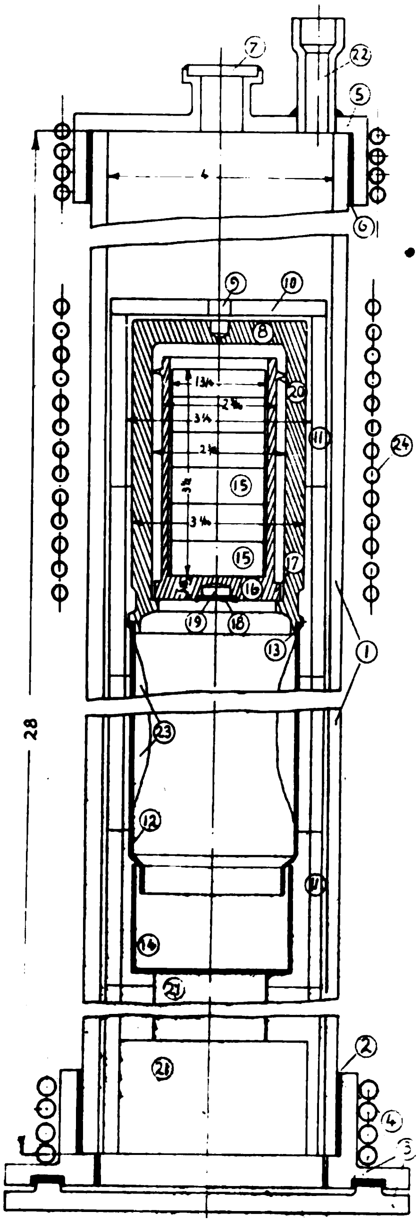

FIGURE 3

1. Quartz furnace tube
2. Picein joint
3. Cover with rubber gasket
4. Rubber gasket
5. Top, water-cooled
6. Picein joint
7. Quartz window
8. Heater shell
9. Hole in quartz plate
10. Quartz cover plate
11. Quartz cylinders
12. Thin sheet-iron condensor
13. Weld joining heater 8 and condensor 12
14. Crucible
15. Briquettes
16. Reaction crucible
17. Bayonet joint
18. Pin
19. Hole in reaction crucible
20. Centering buttons
21. Quartz support
22. Vacuum connection
23. Condensed barium
24. Movable high-frequency coil

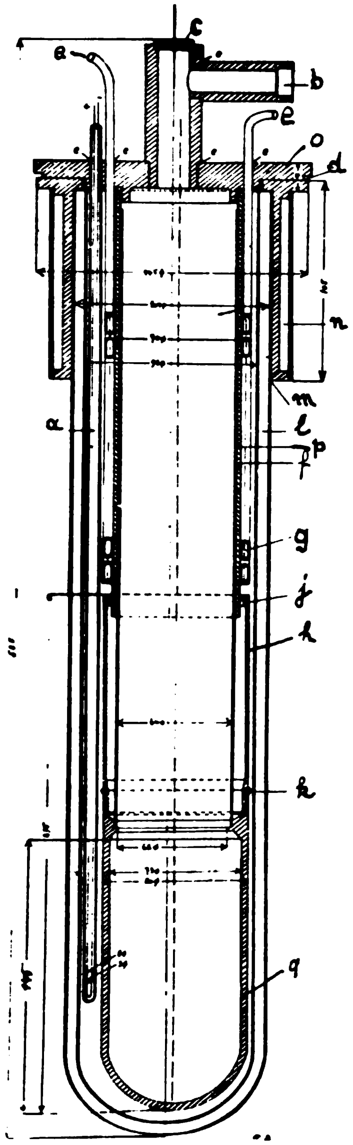

FIGURE 4

l. Furnace tube of Pythagoras porcelain
n. Water-cooled top
m. Picein joint
o. Cover
d. Flat-ground joint
f. Condensor base
g. Flat copper coil
q. Reaction crucible
k. Weld
h. Thin sheet-iron cylinder
j. Bayonet joint
e. Water supply
a. Thermocouple
b. Vacuum connection
c. Quartz window
p. Condensor sheet

Despite the fact that magnesium cannot be used as a reducing agent for $BaCl_2$ to make pure metal, some barium may be introduced into magnesium by using $BaCl_2$ as a flux for BaO and reacting this with molten magnesium. MgO is only slightly soluable in chlorides; therefore only limited amounts of BaO can be reduced to avoid stiffening of the bath by MgO that forms.

BaF_2 can also be reduced with magnesium or aluminum (16), but the high melting point of the fluoride and the fairly low fluorine affinity of aluminum limit the efficiency of this method. However, fluoride may be added when reducing BaO with aluminum to liquefy the melt and raise the Ba content of the alloy.

PRACTICAL APPLICATION OF THE GUNTZ PROCESS

Blitz and Huttig (5), Ruff and Hartmann (72), and Clark (12) describe the small laboratory equipment they used. A more elaborate apparatus is shown in a patent of the I. G. Farbenindustrie (33,77) which warrants discussion. Details of this apparatus are given in figure 2.

The metal is condensed as a liquid and cast from time to time in a cool mold. This, however, can be done only under specific conditions. Condensation must take place above the triple point of barium, which is 0.08 mm. Hg at 710°C., according to an extrapolation made from the curve given by Espe-Knoll (17). This pressure is so low that little barium can escape into those parts of the furnace that are held below 710°C. The dissipation of barium into the cooler parts of the equipment could be prevented by using a noble gas pressure outside the condenser superior to 0.08 mm. Hg; but this hampers slightly the evaporation of barium from the mixture, which takes place at a total pressure of about 2 mm. Hg. It is better to hold the condenser under the pressure of the barium vapor itself, which can be done by keeping it fairly well closed. The condenser temperature has to be above 710°C.; the patent recommends 750° to 800°C. The main purpose of casting in a vacuum is to avoid the formation of Barium nitride or oxide produced when thin layers of condensate are exposed to air on opening the furnace. The low vapor pressure of barium at the triple point causes difficulties when the metal is distilled in a vacuum, owing to the considerable refluxing that takes place when condensing upwards. With barium, downward condensation is always preferable. Refluxing is also observed during the reaction period when reducing BaO and condensing above the batch.

Disagreement exists between different authors regarding the temperature of reduction. Guntz (24) worked at 1,300° to 1,340°C. when reducing BaO with aluminum. Blitz and Huttig (5) claim that 1,010° to 1,050°C. is a suitable temperature. Ruff and Hartmann (72) mention 1,100°C. The writer made many runs in the equipment shown in figure 3 and measured the temperature inside the crucible. Best results were obtained at 1,150°C., but in the apparatus shown in figure 4, to which external heat was applied through a refractory tube, the temperature measured between the tube and the reaction crucible was slightly higher, namely 1,200°C. The crucible, however, may be cooler when the barium evaporates.

Special attention must be paid the barium oxide used in this process. It should be freshly prepared, as otherwise it picks up moisture and CO_2. Depending on the method of preparation, it may contain BaO_2, which causes gas evolution over a long period. The writer made the oxide from precipitated carbonate by mixing with 6 percent lampblack (fuligo) and heating the mixture, which was compressed in a thin sheet-iron crucible under a vacuum at 1,000°C. The reaction starts at 350° and is almost complete within 24 hours. After cooling, the material was again crushed, mixed with 1 percent lampblack, and the operation repeated. This method yields a 98-percent oxide, which is mixed with aluminum grains of about 50 x D in the ratio of 2 mol. BaO for 1 mol.Al, and is pressed into briquets. The vacuum has to be of the highest order. When using a mercury diffusion pump, the use of a liquid air trap is absolutely necessary to avoid contamination of the barium. The first heating up to the flash point (about 1,050°C.) must be done carefully to permit evacuation of residual gases that might react with barium or reduce the yield.

Two examples of our method of operation may be given, the first showing high-frequency heating and downward condensation, and the second, external heating and upward condensation. The first apparatus permitted inputs of 250 gr., the second, about 1,000 gr.

Figure 3 shows the arrangement in the first case. The furnace tube of silica, 1, is sealed in with picein cement; 2, in a water-cooled bottom; 3, provided with a rubber gasket; 4, which permits removal of the cover. The top, 5, is fitted to the furnace tube by a water-cooled picein joint; 6, a silica glass window, 7, is sealed in the top tower to permit optical temperature observation of the heavy iron heater shell, 8, through the hole, 9, in the silica cover plate, 10. A series of short silica cylinders, 11, piled on each other protect the furnace tube, 1, from stray barium and sublimed iron (51). The insert contained in the silica cylinders, 11, is constituted of three sections - the induction-heated, heavy-iron shell, 8, the thin sheet condenser, 12, welded very carefully to the heater at 13, and the removable thin-sheet crucible, 14. The reaction crucible, 16, with the briquetted reaction mixture, 15, is fitted into the heater shell by means of the bayonet, 17, which has three knobs. A special tool (not shown) permits inserting by means of the pin, 18, welded across the hole, 19. Small buttons, 20, center the crucible. Quartz blocks, 21, support the insert. The vacuum is applied through the pipe, 22. The high-frequency induction coil, 24, supplies the required energy. The barium condenses at 23 and can be melted down into the thin-sheet crucible, 14, by moving the furnace coil, 24. All dimensions are given in inches.

The apparatus with upward condensation and direct heating is shown in figures 4 and 5 (dimensions in millimeter). The furnace tube, 1, made of Pythagoras porcelain, has a water-cooled top, n, sealed with picein, m, and provided with a cover, o, which has a flat ground joint, d. The insert, consisting of the thin condenser sheet, p, which fits into the condenser base, f, cooled with water by means of the flat copper coil, g, is screwed to the cover, o. The reaction crucible with the mixture, c, is carefully

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welded at k to a thin sheet cylinder, h, provided with the bayonet j, which makes the removable joint with the upper insert. Water is supplied through e. A thermocouple, a, is inserted in the space between the Pythagoras tube and the crucible. A slight eccentricity permits creation of this space. The vacuum connection is at b. The inside of the crucible can be observed through the silica-glass window, c. The condenser sheet, p, fits tightly with the crucible. Any stray barium vapors may condense on the cylinder h. None was ever found on the bayonet. The apparatus is suspended in the large carbon tube resister furnace, so that the Pythagoras tube is not subjected to any other strain than that caused by the atmospheric pressure. The wall temperature may reach 1,350°C.

The following results were obtained: With 900 grams of BaO and 90 grams of Al powder, 345 grams of barium was recovered as an average of 10 runs. This represents a consumption of 2.6 pound of BaO per pound of Ba produced. The aluminum efficiency is slightly above 50 percent, and the Al consumption is 0.26 pound per pound Ba produced. On a still larger scale, using a mixture of 54 parts BaO and 6.5 parts aluminum, a 60-percent aluminum efficiency was obtained. One pound barium produced required about 2.2 pounds of BaO and 0.21 pound of aluminum.

The recovery of barium metal, although not as complete as that of magnesium in the dolomite-silicon process, may still be improved. However, part of the barium oxide has to be sacrificed for the formation of Al_2O_3. BaO, whereas in the dolomite-silicon process, lime replaces magnesia in this role. The barium reaction mixture contains much more theoretically available barium than the dolomite-silicon mixture contains theoretically available magnesium. The figures are 61.5 percent for barium, compared with 22 percent for magnesium. Therefore, the cost of furnace operation is lower per pound of Ba metal than it is per pound of magnesium metal. Taking into account today's prices for the raw materials, barium could be made at less than 45 cents a pound when operations are on a really large scale. Barium sells today in small lots at $15 a pound.

CONCLUSIONS

From a review of the literature on the chemistry of the Guntz process for making barium by reduction of BaO with either Si or Al, it is concluded that when silicon is employed as the reducing agent, orthosilicate is formed, whereas in aluminum reduction, monoaluminate is produced. Diffusion of BaO towards the reducing agent rules the speed of the operation. The formation of intermetallic compounds is analyzed, and it is shown that with barium the reaction goes by the way of silicide or aluminide, whereas this is not yet ascertained with respect to dolomite reduction with aluminum or silicon. A number of other possible vacuum reactions are examined. The dissociation of barium alloys in a vacuum is discussed. Barium alloys can readily be made, either by direct reduction (Si,Al) of the oxide or by reduction of the chloride (Ca) or fluoride (Al) or chloride oxide mixtures (Mg), or by sodium reduction of the chloride in the presence of heavy or light metals. The fusion electrolysis also yields alloys of lower grade. However, none of these methods can be used for

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making barium metal suitable for getter, either because the alloys are stable in a vacuum or because they contain chlorides that can not be removed. The aqueous electrolysis also permits producing alloys of barium with mercury, but the total removal of mercury from such alloys is not possible. Attention should be given the multiple equilibrium reactions between alkali, alkaline-earth metal chlorides, and any metal of these groups alone, or in the presence of or in solution in light or heavy metals, which very generally yield alloys otherwise difficult to prepare. Two apparatuses tested by the author for making barium by the Guntz process are described - one with high-frequency heating and downward condensation and the other with external heat application and upward condensation. The best results obtained show a consumption of 2.2 parts of BaO and 0.21 parts of Al per part of Ba produced. Based upon the siliconthermic distillation plants operated for production of magnesium from dolomite, barium probably could be made on a very large scale at a cost of less than 45 cents per pound.

The chemical methods for making alloys would compete on this cost basis. This should be a stimulant for looking after new commercial uses of elemental and alloyed barium.

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